Nucleophilic and Radical Addition of H_2S to Methyl Linolenate and Linseed Oil[1]

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ABSTRACT

Hydrogen sulfide was added to methyl linolenate and linseed oil to yield mercapto, thio, and thiolan derivatives. Nucleophilic conditions at low temperatures gave faster and more complete reactions than did free radical conditions. Major reaction products were identified by gas liquid chromatography, mass spectrometry, and nuclear magnetic resonance. Nucleophilic addition of hydrogen sulfide to the methyl esters of hydrogenated nonconjugatable linseed oil was made at -70 C in the presence of boron trifluoride, and thiolan derivatives appeared to form in preference to thiane derivatives.

INTRODUCTION

Previously we (1,2) described the addition of hydrogen sulfide to methyl oleate and methyl linoleate by free radical and nucleophilic mechanisms. Gunstone (3) has also reported on the preparation and properties of some saturated and unsaturated mercapto C_{18} esters and related compounds. Our search for fatty organosulfur compounds useful as coatings and lubricant additives has been extended to include the hydrogen sulfide adducts of methyl linolenate and linseed oil. The results of these studies are the subject of this paper.

EXPERIMENTAL PROCEDURES

Starting Materials

Methyl linolenate (all *cis*) obtained from the Hormel Institute (Austin, MN) was 99% pure by gas liquid chromatographic (GLC) analysis. Hexane was redistilled Skelly B (bp 67-70 C) obtained from the Skelly Oil Company (Kansas City, MO). Alkali refined linseed oil (Superb) was received from Archer Daniels Midland Company (Decatur, IL). Hydrogen sulfide and boron trifluoride were Matheson CP grades. Benzene was "Baker Analyzed" reagent grade.

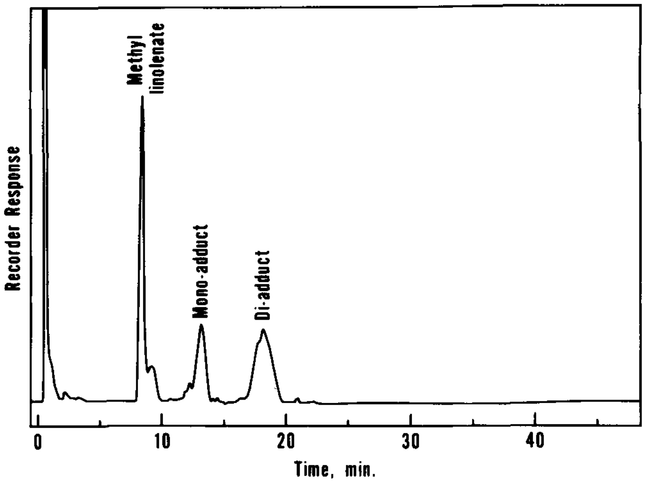

FIG. 1. Gas liquid chromatography (GLC) of H_2S adduct of methyl linolenate after 48 hr irradiation at 25 C.

Methyl Esters of Hydrogenated Nonconjugatable Linseed Oil

Alkali-refined linseed oil (300 g) was hydrogenated with a highly active copper catalyst (4) at 170 C and 600 psi until no further hydrogen uptake. Super Filtrol (10 g) was added and the oil was vacuum filtered. Yield, 314 g; iodine value, 122.8; acid value, 0.57; nonconjugatable diene, 47.9%; oleic, 38.6%; palmitic, 6.2%; stearic, 4.3%; conjugatable diene, 2.9%. Nonconjugatable unsaturation was determined by the 6.6% KOH-25 min conversion AOCS method (5) and by GLC analysis. Hydrogenated nonconjugatable linseed oil (97 g), methanol (100 ml), and sodium methylate (0.5 g) were refluxed for 2 hr and glacial acetic acid added until the mixture was slightly acid to litmus paper. The excess methanol was removed by distillation; petroleum ether (100 ml) was added; and the product was washed with distilled water (100 ml) and dried over anhydrous sodium sulfate. Yield, 73 g.

Addition of Hydrogen Sulfide to Methyl Esters and Linseed Oil

The photochemical apparatus and procedure has been described previously (6). A medium pressure mercury vapor lamp (Hanovia 8A36) was used and the apparatus was charged with 300 ml (264 g) of thiophene-free benzene and saturated with hydrogen sulfide (Matheson CP grade). Solubility of hydrogen sulfide in benzene at 25 C is 0.01088 g/g (7), so the solvent contains 2.87 g (0.084 mole) of hydrogen sulfide. Between 5 and 10 g of linseed methyl esters or oil was used in the irradiations. For 8 g (0.0269 mole) of methyl linolenate there is approximately a threefold excess of hydrogen sulfide in solution. Hydrogen sulfide was introduced continuously (2 bubbles/sec) during the experiment to maintain a saturated solution.

Nucleophilic additions were similar to those described previously (2) for the addition of hydrogen sulfide to methyl oleate, methyl linoleate, and soybean oil. Two-gram samples were dissolved in 150 ml of hexane instead of the 1 g/20 ml previously used. A Premier 1-in. Dispersator was used in place of the Teflon-coated magnet, and a Pyrex tube (8 in. x 2-3/8 in.) replaced the 100 ml graduate. No changes were made in treatment after completion of the reaction.

Sample Collection and Analytical Procedures

Samples separated by GLC were collected in 2 in. No. 14 Teflon tubes inserted at the exit port of a Hewlett-Packard Model 7620A research chromatograph. Program runs were conducted on a 6 ft x 1/4 in. 3% JXR column at 180-300 C usually with a heating rate of 4 C/min and a helium carrier gas flow of 30 cc/min. This instrument was fitted with a microsplitter-collector that provided a 1:10 split ratio (1 part to the flame ionization detector and 10 parts to the collector tubes). Samples were rechromatographed to increase purity.

Mass spectra were measured on a Nuclide 12-90-DF mass spectrometer equipped with an all-glass inlet; inlet temperature, 200 C; source temperature, 200 C; and 70 V electron energy.

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[1] Presented at the AOCS meeting, Cincinnati, September 1975.

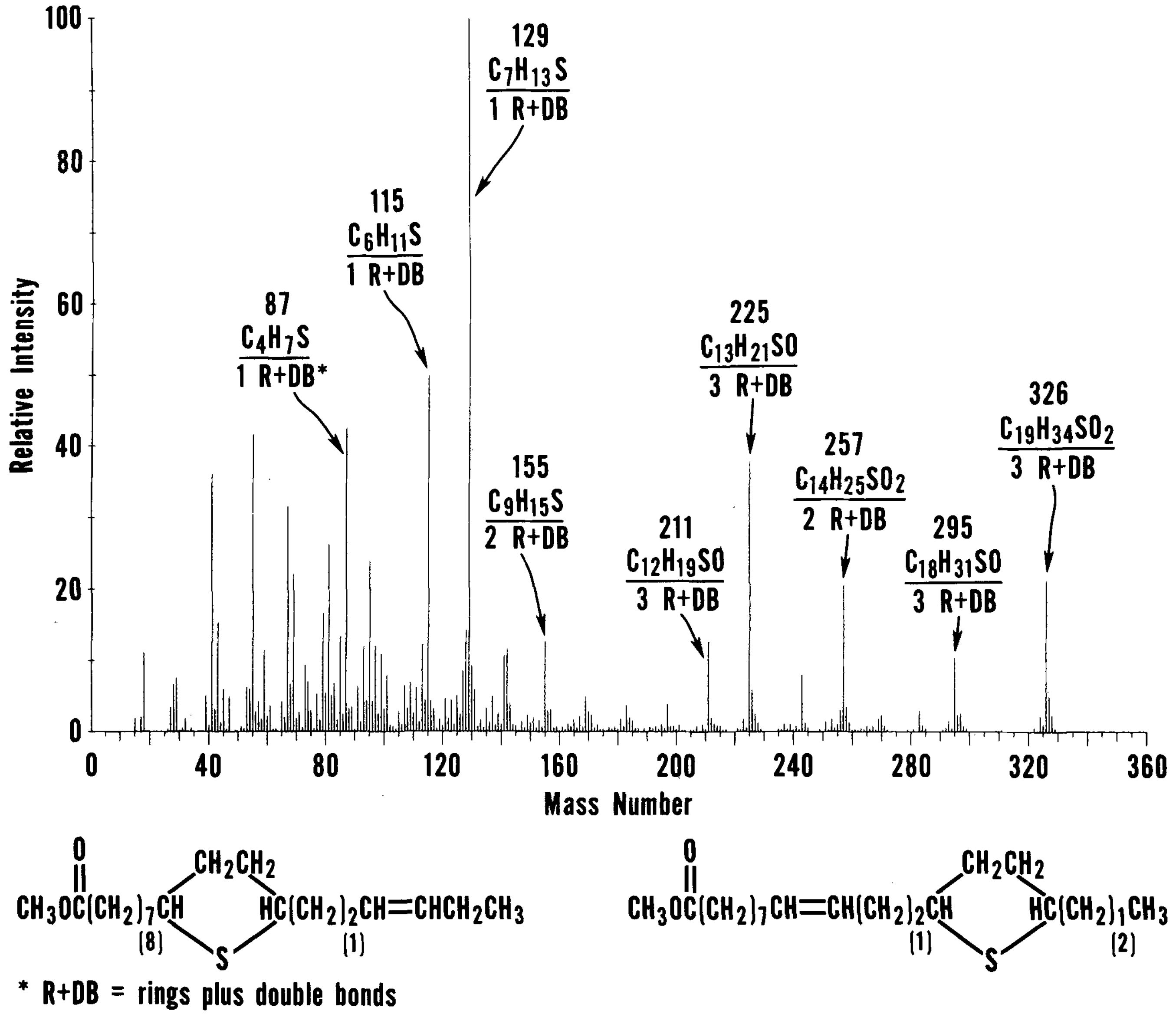


FIG. 2. Mass spectrum of preparative gas liquid chromatographic (GLC) mono-adduct of H_2S and methyl linolenate with underlined chemical formulas obtained by high resolution peak matching.

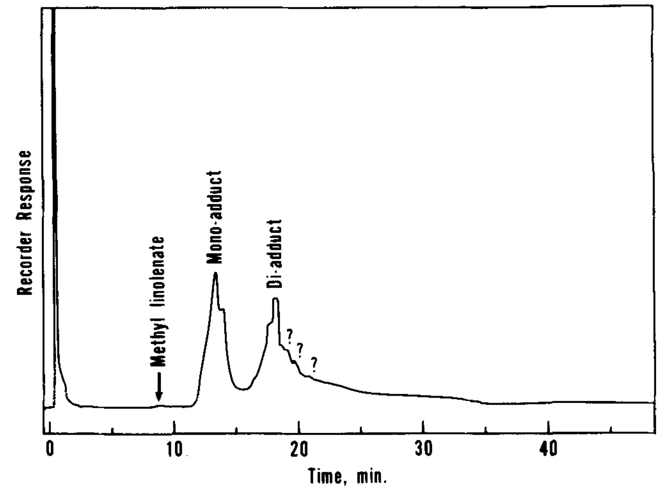


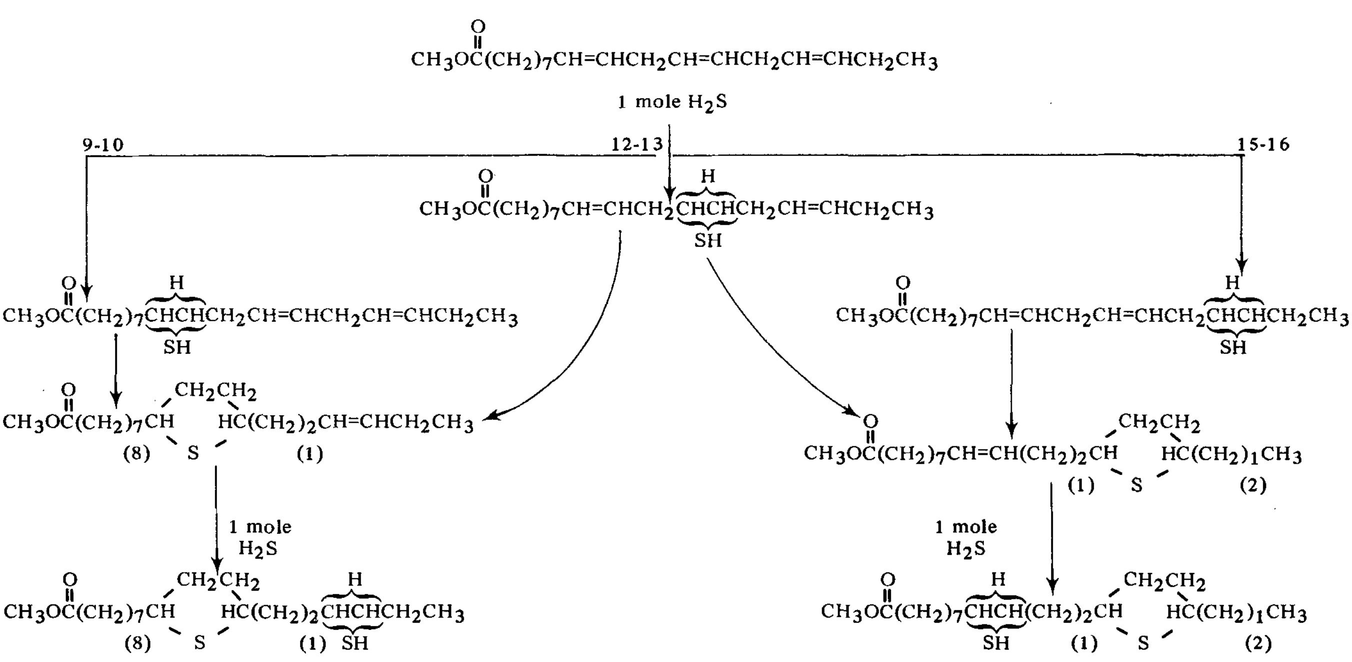
FIG. 3. Gas liquid chromatography (GLC) of H_2S adduct of methyl linolenate after 4 hr with BF_3 at -70 C.

RESULTS AND DISCUSSION

Hydrogen Sulfide Adducts of Methyl Linolenate

A GLC of the reaction product of methyl linolenate and hydrogen sulfide after 48 hr of ultraviolet irradiation is shown in Figure 1. When an internal standard (lauryl mercaptan) is added, GLC analysis shows that 90% of the reaction product emerged from the column. Approximately one-half of the sample was methyl linolenate and elaidinized methyl linolenate and the remaining half was distributed nearly equally between two principal groups of product peaks composed of mono and di adducts. Preparative gas chromatography of the sharp high point from the mono adduct group and mass spectrometry (Fig. 2) of this sample showed a product with a mol wt of 326. The mass spectrum has underlined molecular formulas obtained by high resolution mass spectrum peak matching. These mass peaks were determined to one millimass, and sulfur was detected in all of the principal peaks (326, 257, 225, 211, 155, 129, 115 and 87). During high resolution peak matching, the usual oxygen fragments $[(CH_2)_n\ COOCH_3]^+$ were looked for adjacent to the sulfur peaks. None of the oxygen peaks were found except at mass 87 which had a $C_4H_7O_2$ peak 10% of the C_4H_7S peak. The m/e 87 is accountable by the cyclic five-membered ring $(CHCH_2CH_2CH_2S=)^+$ arising from α-cleavage of the structures listed below the

Scheme I



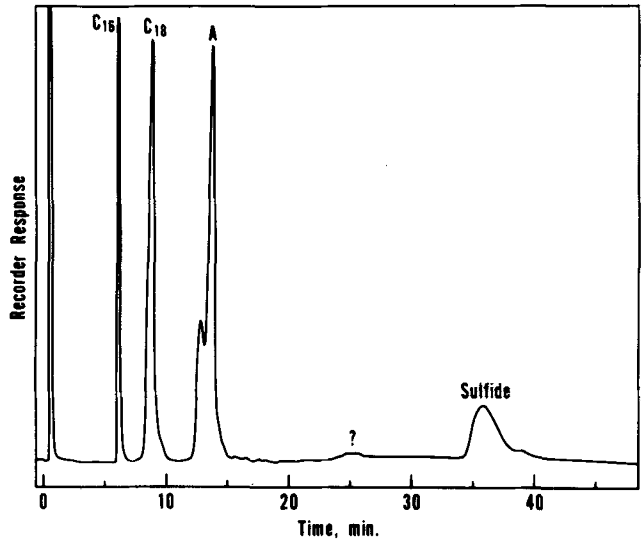


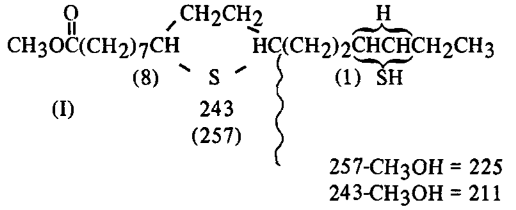
FIG. 4. Gas liquid chromatography (GLC) of H_2S adduct of methyl esters of hydrogenated nonconjugatable linseed oil after 4 hr with BF_3 at -70 C.

spectrum. The initial reaction is probably an addition of hydrogen sulfide to the 9-10, 12-13 and 15-16 positions which is followed by intramolecular cyclization via Scheme I.

Because of large differences in the size of fragments and because one fragment contains a double bond, it is not possible to determine the relative amounts of isomers from mass spectra data without the use of necessary standards, which are not available.

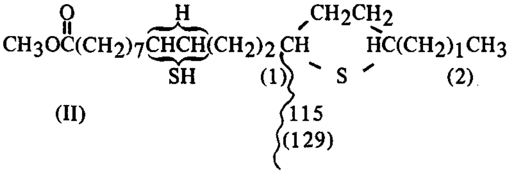
The major component from the second group of products (Fig. 1) was collected and had a mol wt of 360 indicating products where 2 moles of hydrogen sulfide added to methyl linolenate (Table I). This fraction is probably a mixture of methyl 9,12-epithio-15(16)-mercaptostearate; methyl 10,13-epithio-15(16)-mercaptostearate; methyl 12,15-epithio-9(10)-mercaptostearate; and methyl 13,16-epithio-9(10)-mercaptostearate. The fragmentation peak at 327 accounts for loss of an SH which is common for secondary mercaptans (8). Fragment 295 is the result of loss of methanol from the 327 fragment. Peaks at 211, 225, 243 and 257 are attributed to the degradation of structure I:

(I)



while the fragment peaks 115 and 129 are accountable from structure II:

(II)

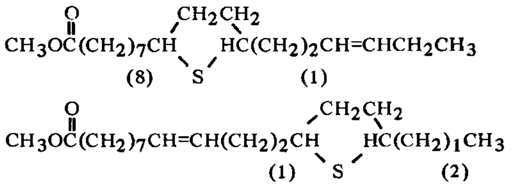
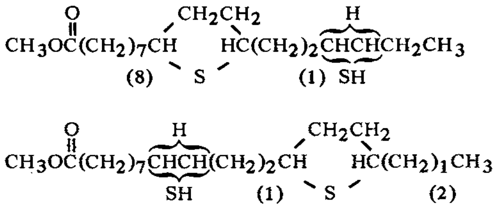
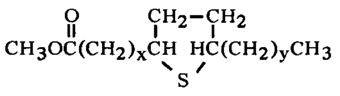
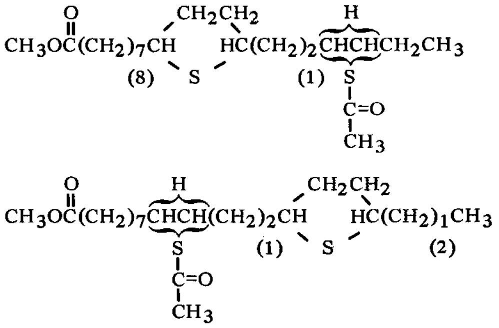


Nuclear magnetic resonance (NMR) data on the dihydrogen sulfide adduct before actylation shows a characteristic signal at 7.2-7.4 τ for the methine H on the carbon with the mercapto group. After acetylation this signal disappears but a singlet at 7.7 τ appears which is characteristic of $SCOCH_3$ (3). Another characteristic signal present in both spectra is 6.6-6.8 τ which is attributed to the methine H on the 2 and 5 atoms of the disubstituted thiolan. Mass spectral analysis for the acetylated product shows a principal peak of 359 (Table I). This peak represents M - 43 or loss of acetyl group which is a commonly eliminated fragment.

GLC analysis of the BF_3-catalyzed addition of hydrogen sulfide to methyl linolenate after 4 hr at -70 C is shown in Figure 3. Only a small amount of unreacted methyl linolenate remains, and this is in contrast to ca. 50% of unreacted (and elaidinized) methyl linolenate in the photochemical reaction after 48 hr (Fig. 1). One major reaction product is the adduct of 2 moles of hydrogen sulfide to 1 mole of methyl linolenate, but there is a considerable amount of unidentified reaction products not yet charac-

TABLE I

Mass Spectral Data on H_2S Adduct of Methyl Linolenate and Methyl Esters of Linseed Oil

Compound	Formula	Spectral data
Mono-H_2S adduct of methyl linolenate and methyl esters of linseed oil		Mass 326(18), 295(10), 257(19), 243(7), 225(32), 211(9), 129(100), 115(40)
Di-H_2S adduct of methyl linolenate and methyl esters of linseed oil		Mass 360(31), 327(100), 295(22), 257(9), 243(9), 225(9), 211(9), 129(22), 115(39)
Mono-H_2S adduct of methyl esters from non-conjugatable linseed oil	 x + y = 12	Mass 328(17), 297(14), 257(19), 243(19), 225(25), 211(21), 199(15), 171(56), 157(67), 129(44), 115(38)
Acetylated di-H_2S adduct of methyl linolenate		Mass 359(M - 43,100) 327(28), 295(9), 257(4), 243(5), 225(6), 211(8), 155(6), 141(11), 129(16), 115(31)

terized which emerge from the column after the di adduct. When an internal standard (lauryl mercaptan) is added, GLC analysis shows that ca. 80% of the reaction product is volatile on GLC.

Hydrogen Sulfide Adducts of Linseed Oil and Methyl Esters of Hydrogenated Nonconjugatable Linseed Oil

Addition of hydrogen sulfide to linseed oil and its methyl esters showed products similar to those identified from methyl linolenate along with sulfur derivatives from methyl oleate and linoleate; namely, methyl 9(10)-mercaptostearate and the mixture of methyl 9-(2-pentyl-1-thiolan-5-yl)nonanoate and methyl 8-(2-hexyl-1-thiolan-5-yl)octanoate.

Figure 4 is a GLC of the product obtained from the nucleophilic addition of hydrogen sulfide to the methyl esters of hydrogenated nonconjugatable linseed oil (9) at -70 C in the presence of boron trifluoride. Addition of an internal standard (dodecyl sulfide) shows ca. 80% volatiles. Preparative GLC of one of the principal reaction products (peak A, Fig. 4) shows a mass spectrum (Fig. 5) with a parent peak of 328 and has a fragmentation pattern similar to that from the hydrogen sulfide adduct of methyl linoleate (2). The hydrogen sulfide adduct of a nonconjugatable diene such as methyl 9,13-octadecadienoate would permit a thiolan from a 10-13 cyclization. Other cyclizations 9-13 and 10-14 would yield a thiane derivative. The relative intensities of 87 and 101 mass peaks suggest that the thiolan appears to form in preference to the thiane compound. Position of the thiolan ring along the chain is not certain from mass spectra data. Isomerizations can occur through either a cyclic sulfenium ion or a carbonium ion (2). These results are consistent with ring closure studies of sulfure halides that show the relative rates of formation of five, six, and seven-membered rings to be 6000:76:1 (10).

ACKNOWLEDGMENTS

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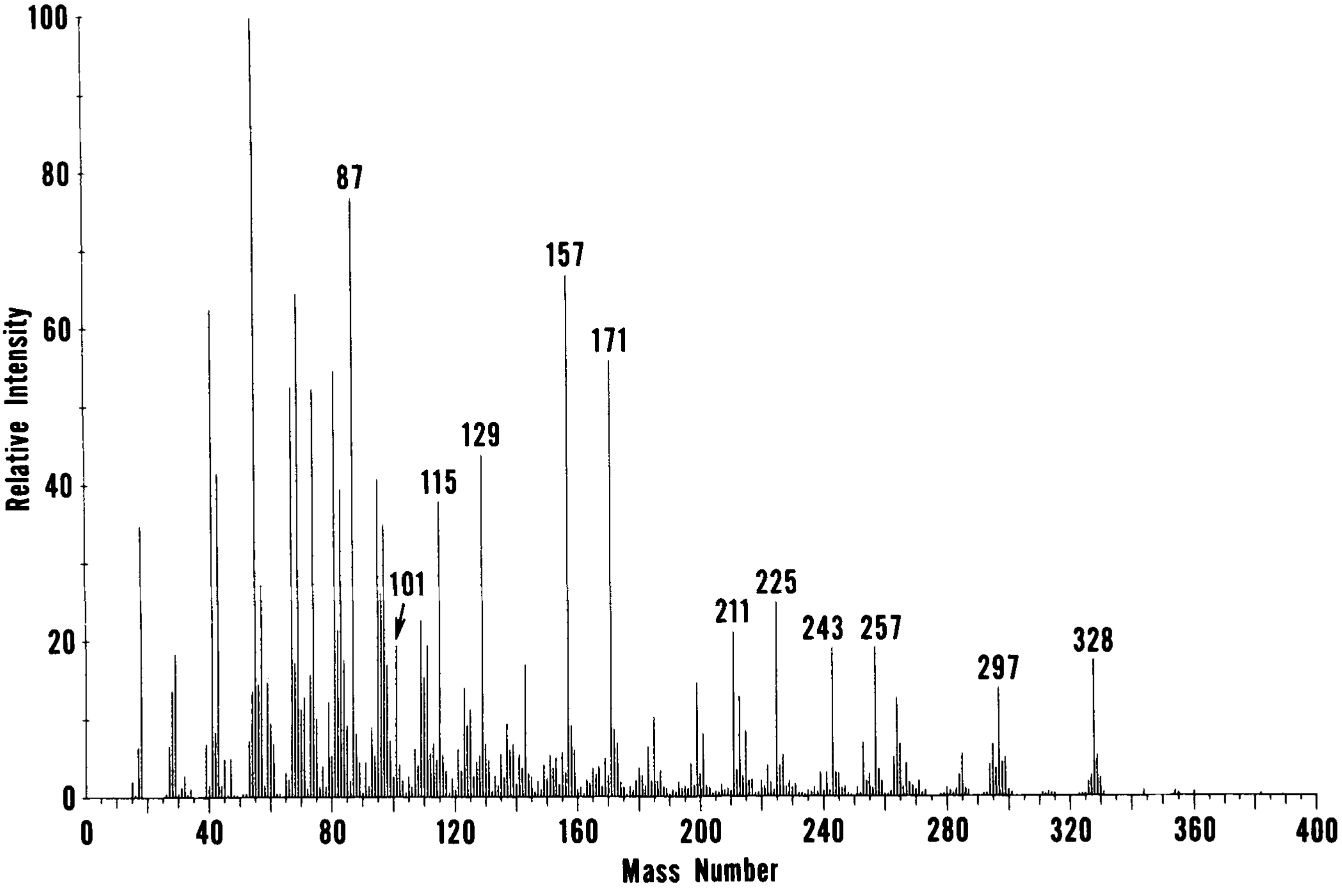

FIG. 5. Mass spectrum of a preparative gas liquid chromatographic (GLC) H_2S adduct of methyl esters from hydrogenated nonconjugatable linseed oil.

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